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Simplified Reference Electrode for Electrorefining of Spent Nuclear Fuel in High Temperature Molten Salt

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SIMPLIFIED REFERENCE ELECTRODE FOR ELECTROREFINING OF SPENT NUCLEAR FUEL IN HIGH TEMPERATURE MOLTEN SALT

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Pyrochemical processing plays an important role in development of proliferation-resistant nuclear fuel cycles. Electrorefining in a high temperature molten salt is considered a signature or central technology in pyroprocessing fuel cycles. Reference electrodes provide information essential for monitoring the reactions occurring at the electrodes, investigating separation efficiency, controlling the process rate, and determining the process end-point. Vycor-glass design reference electrodes have provided good durability and signal stability, but are not easily fabricated. The design is a complex construction involving multiple small pieces, glass joints, ceramic to glass joints, and ceramic to metal joints all assembled in a high purity inert gas environment. A simpler design, based on an ion-permeable membrane of mullite has been completed. The new design maximizes the use of commercial components, reduces assembly piece count more than one-half, and can be fabricated with less specialized skills. This has resulted in a significant reduction of effort and cost to fabricate replacements. The new design has been tested in a lab scale electrorefiner and has also been successfully scaled up and installed in engineering scale electrorefiners.

INTRODUCTION

The Idaho National Laboratory currently operates two engineering scale electrorefiners demonstrating pyroprocessing technology at its Materials and Fuels Complex. The two batch mode electrorefiners (ERs), identified as Mark-IV and Mark-V versions, process irradiated fuel elements from the Experimental Breeder Reactor-II. The electrorefining process is conducted at a temperature near 500^o C in a molten lithium-chloride/ potassium-chloride (LiCl/KCl) salt pool.

The ERs are cylindrical chrome-moly (2.25% Cr – 1% Mo) steel vessels with an inside diameter of 1-m (40-inches) and height of 1-m (40-inches). Four 25.4-cm (10-inches) diameter ports on top of the vessels permit access for the anode and cathode assemblies. Figure 1 is a simplified illustration. The Mark-IV version processes primarily driver fuel in a nominal 33-cm (13-inch) layer of molten LiCl-KCl eutectic on top of a nominal 15-cm (6-inche) layer of molten cadmium (Cd). The LiCl-KCl eutectic contains approximately 10 wt% of uranium-chloride (UCl_3). By contrast, the Mark-V processes blanket fuel in a single nominal 42-cm (19-inches) deep layer of the same eutectic salt.[1,2]

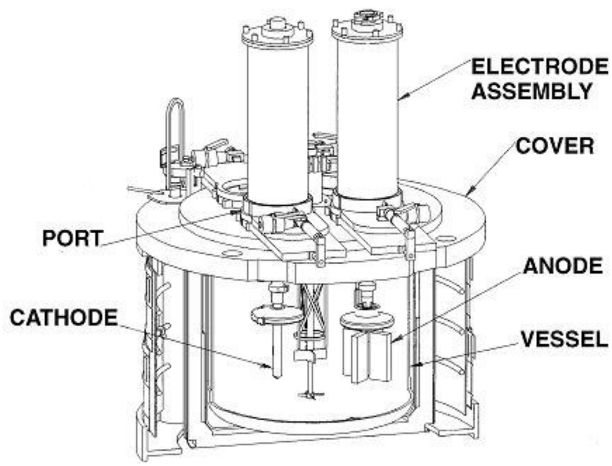

Figure 1: Simplified Section View of Electrorefiner

ELECTROREFINING PROCESS

The following process details of the Mark-IV version are illustrative of both systems. The spent driver fuel, which serves as feedstock for the Mark-IV, consists of uranium (U), zirconium (Zr), bond sodium, and fission products all within a stainless steel cladding. A typical batch contains the segments from two or three chopped spent fuel assemblies. A fuel assembly consists of 61 fuel pins with nominally 4.1-kg (9-lb) U, .6-kg (1.2-lb) Zr, and other fuel components. The primary purpose of electrorefining is to separate actinides from other fuel components. Once the anode is loaded with chopped fuel segments and inserted in the electrolyte, the bond sodium and active metal fission products chemically react and displace UCl_3 from the molten salt. The U metal from the displacement may form on the fuel segment surfaces or disperse into the salt and settle into the Cd pool. The U in the fuel segments is electrochemically dissolved, transported through the salt, and deposited onto the cathode. The Zr and noble metal fission products are ideally retained in the cladding hulls.

REFERENCE ELECTRODE FUNCTION

Two silver/silver-chloride (Ag/LiCl-KCl-1wt%AgCl) reference electrodes installed in the salt phase of each ER monitor the electrical potential between the salt pool, the cathode, and the anode. Figure 2 is a simplified diagram illustrating typical electrical connections. The reference voltage signals provide real-time information on the electrochemical processes occurring at the electrode/salt interfaces. It is key information to the study of the process and a primary input to control the dissolution, deposition, and transport of actinides and fission products in the systems.

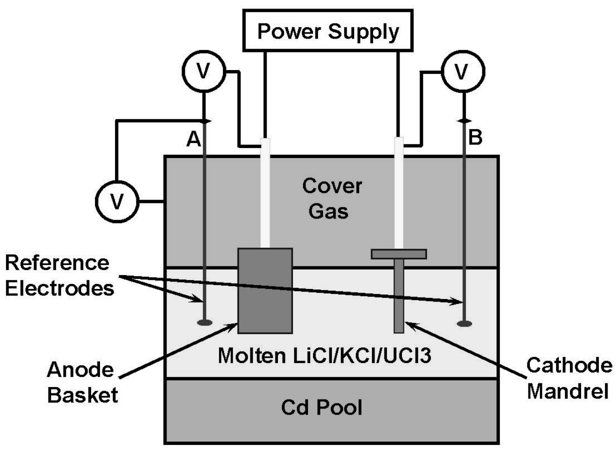

Figure 2: Simplified Electrical Diagram

For example, in the Mark-IV, the measured voltage difference between the reference electrodes and the ER vessel represents the voltage difference between the reference electrodes and salt/Cd interface. Since the concentration of UCl3 in the electrolyte is kept relatively constant at approximately 10 wt%, the variations in the reference electrode readings actually reflect the variations of U concentration in the molten Cd. The standard Nernst Equation can be used to calculate the reference electrode voltage versus U concentration in the molten Cd.

In the Mark-IV system, the predominant electrochemical reaction at salt/Cd interface at equilibrium is:

$$U^{3+} + 3^{e-} \leftrightarrow U_{(Cd)} \qquad (1)$$

By the Nernst Equation, the measured reference electrode reading represents:

$$\Delta V_{Cd-ref} = E^0{}_{U^{3+}} + \frac{RT}{3F}\ln\frac{a_{U^{3+}}}{a_{U(Cd)}} - (E^0{}_{Ag^+/Ag} + \frac{RT}{F}\ln_{a_{Ag^+}}) \qquad (2)$$

$$\Delta V_{Cd-ref} = (E^0{}_{U^{3+}/U} - E^0{}_{Ag^+/Ag} - \frac{RT}{F}\ln a_{Ag^+} + \frac{RT}{3F}\ln a_{U^{3+}} - \frac{RT}{3F}\ln\gamma_{U(Cd)}) - \frac{RT}{3F}\ln c_{U(Cd)} \qquad (3)$$

Term a_U^{3+} is the U^{3+} activity in the salt phase, a_{Ag}^+ the Ag^+ activity in the reference electrode, $a_{U(Cd)}$, $\gamma_{U(Cd)}$, and $c_{U(Cd)}$ are the U activity, U activity coefficient, and U concentration in the liquid Cd, respectively. Since the items in the parentheses are constant at a given temperature, equation (3) can be re-written as:

$$\Delta V_{Cd-ref} = A - \frac{RT}{3F}\ln c_{U(Cd)} \qquad (4)$$

Term A is constant at the ER operational temperature. The solubility of U metal in Cd at 500°C is 1.124 x 10^{-2} mole percent, and the activity of U in the molten Cd at saturation is unity. Therefore, the constant A can be determined experimentally by measuring the reference electrode voltage when the Cd pool is saturated with U. This yields an A value of -1.30 V. When the U concentration in the molten Cd is below saturation, the reference electrode reading will thus be:

$$\Delta V_{Cd-ref} = -1.3 - \frac{RT}{3F}\ln c_{U(Cd)} \qquad (5)$$

The ΔV_{Cd-ref} determined by equation (5) has been used to estimate U concentration in the Cd for the ER operations. Figure 3 shows the measured ΔV_{Cd-ref} versus the U concentration in the Cd pool. The ΔV_{Cd-ref} calculated by Equation 5 is also plotted in the figure for comparison. It can be seen that the measured ΔV_{Cd-ref} agrees well with the predicted values.[3]

REFERENCE ELECTRODE DEVELOPMENT AND PERFORMANCE

The Ag/AgCl reference electrode was the result of development work from the 1980s. The electrode demonstrated good life expectancy and signal stability, but is not easily fabricated. It consists of an ion-permeable membrane that allows a potential to be established between the electrode wire terminating in electrolyte inside the membrane and electrodes terminating in electrolyte outside the membrane. Original membrane materials investigated included vycor glass, quartz, mullite, zirconia, and alumina in two different electrolyte molten salt mixtures. A salt of barium/calcium /lithium/sodium-chloride (BaCl/CaCl2/LiCl/NaCl) was used to study zirconium transport and a salt of LiCl/KCl was used to study uranium transport. The vycor glass membrane was the most promising, though the combinations tested were not exhaustive. In particular, mullite was only tested in the BaCl/CaCl2/LiCl/NaCl salt system.

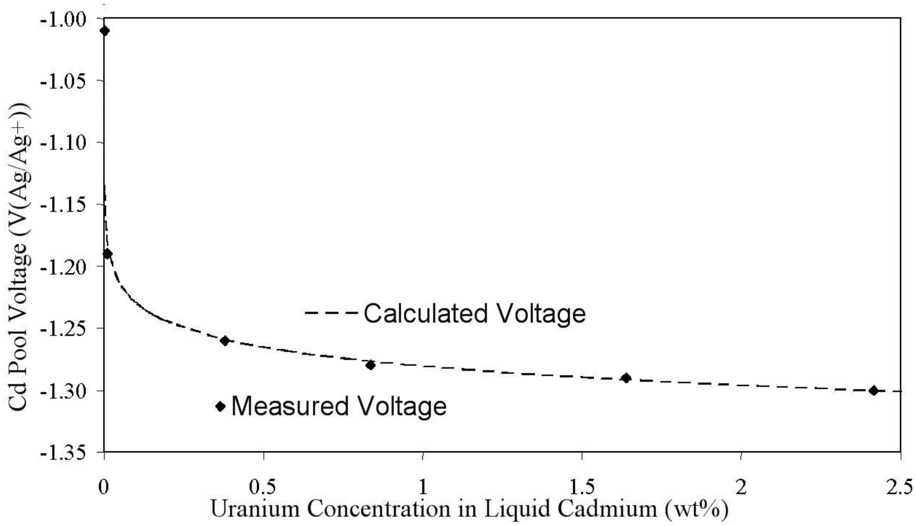

Figure 3: Measured Reference Electrode Voltage Compared to Calculated

Erratic performance was noted in the first two tests when the silver electrode wire was allowed to touch the inside of the membrane. To solve this problem, a slotted alumina tube was used to fix the position a loop of silver wire in the electrolyte without touching the inside membrane surface. This coupled with a configuration requiring assembly of multiple ceramic to glass or ceramic to metal joints assembled in a high purity inert gas atmosphere made fabrication difficult. Figures 4, 5, and 6 show some of the complex construction details. As the electrodes reached end-of-life it was uncertain if the original fabrication knowledge had been sufficiently captured to successfully fabricate replacements without considerable trial and error. At best, the complexity and high level of skill required would make the electrodes very expensive.

Bench scale test equipment known as the hot fuel dissolution apparatus located in an inert atmosphere hotcell is used to support pyroprocessing development. Here small scale tests involving actual spent fuel can be setup and conducted. The equipment is flexible and can be configured to operate as an electrorefiner. A simple, stable, and easily implemented reference electrode was needed for this equipment.

A simplified mullite membrane showed promise when used in LiCl/KCl electrolyte. Table 1 compares the material properties of mullite to vycor.[4,5] Mullite has better temperature characteristics that contribute to improved thermal shock capacity and durability.

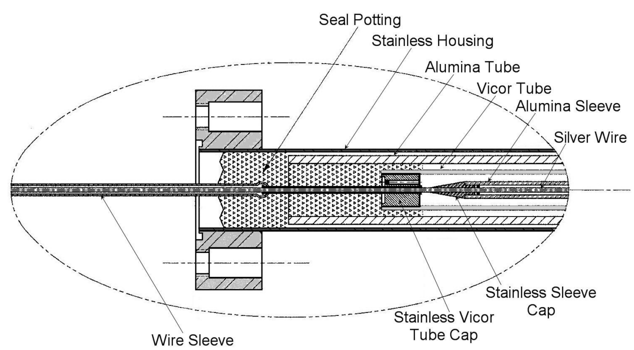

Figure 4: Top Detail of Reference Electrode

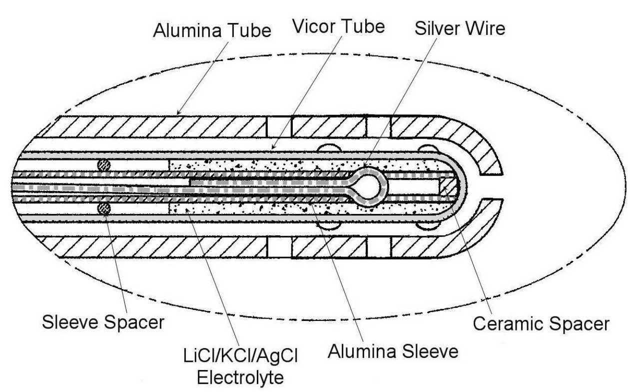

Figure 5: Bottom Detail of Reference Electrode

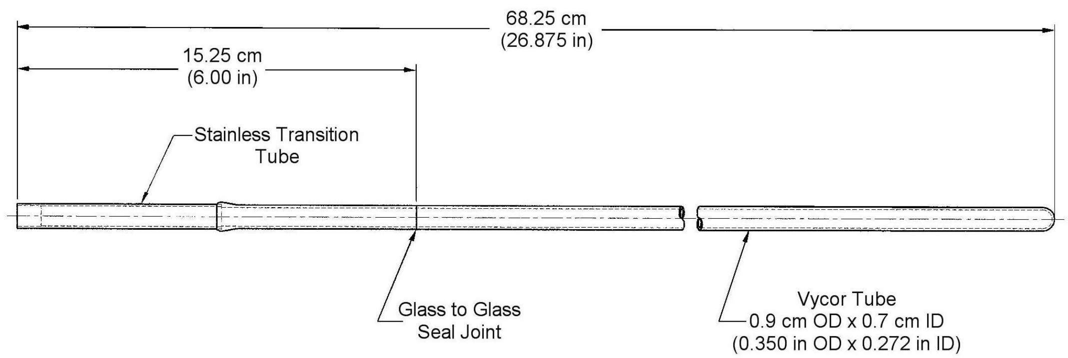

Figure 6: Vycor Tube Detail

Table 1: Material Property Comparison

Material	Thermal Expansion	Density	Youngs Modulus
Vycor	7.5×10^{-7} /°C	2.18 g/cc	6.62×10^{10} Pa
Mullite	5.3×10^{-7} /°C	2.8 g/cc	15×10^{10} Pa

Prototypes provided good signal stability even when the silver electrode wire was allowed to contact the inside of the membrane. Standard off-the-shelf mullite tubes normally used for thermocouple wells were purchased for the electrode bodies. The tubes are closed on one end with a collar on the open end suitable for mounting. A ceramic spacer was used to help position the silver wire in the salt electrolyte and the wire was potted in place at the top of the open end. With the improved material performance no additional protection tubes were used. Using standard off-the-shelf configurations allowed reduction in piece count and simplification in assembly. All these factors contribute to making a reference electrode that is not only cheaper and easier to fabricate, but one that is more robust. Figure 7 illustrates the simplified final design. Several electrodes were used in various bench scale experiments lasting up to 10-months in duration. Signal stability was found to be ± 5-mV.

With this success, a configuration was designed for the engineering scale ERs. Because of electrode length, a full length alumina sleeve is still used to hold the silver wire in the bottom of the electrode and ensure immersion in the salt electrolyte. There is no need, however, to prevent the silver wire from contacting the inside surface of the mullite. The first redesigned electrode was installed in November 2005 in the Mk-V ER. Two more reference electrodes were installed in the Mk-V and Mk-IV ERs in 2006. To date the electrodes continue to function with satisfactory performance.

SUMMARY

A simplified reference electrode design based on an ion-permeable membrane of mullite has been demonstrated. The new design uses the same high purity silver wire as the electrode and the electrolyte composition remains the same. Use of commercial components has reduced the need for specialized fabricating skills and the risks associated with successfully fabricating complex assemblies. Assembly piece count has been reduced. Replacement costs have been reduced. The mullite is a more robust material and signal stability has not been reduced.

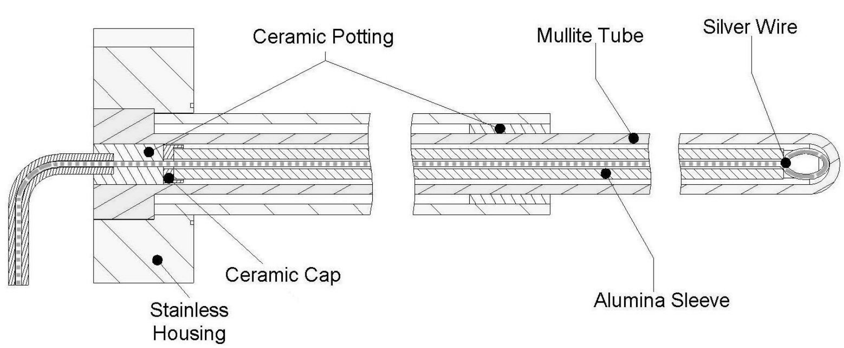

Figure 7: Simplified Electrode Design

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